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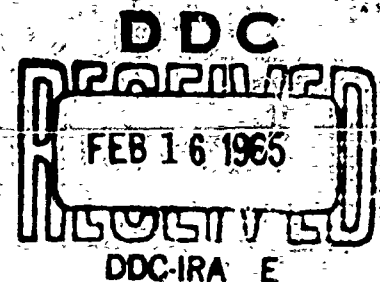
SACRAMENTO PLANT

INVESTIGATIONS OF THE MECHANISMS OF DECOMPOSITION, COMBUSTION, AND DETONATION OF SOLIDS

Report No. 0372-01-20Q

January 1965

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AEROJET-GENERAL CORPORATION
SACRAMENTO, CALIFORNIA

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INVESTIGATIONS OF THE MECHANISMS
OF DECOMPOSITION, COMBUSTION, AND DETONATION
OF SOLIDS

A Report to
Director of Aeronautical Sciences
Air Force Office of Aerospace Research

CONTRACT AF 49(638)-851
OSR Project No. 9750, Task 37501
ARPA Order No. 24-60, Project No. 4759

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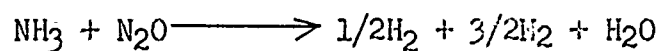
Report No. 0372-01-20Q

This is the twentieth quarterly Technical Operating Report submitted in partial fulfillment of the contract. It covers the period 1 October through 31 December 1964.

C. J. Strickler for
L. J. Rosen, Assistant Manager
Propellant Research Division
Solid Rocket Operations

ABSTRACT

The overall stoichiometry of the $\text{NH}_3\text{-N}_2\text{O}$ counter-flow diffusion flame has been determined from mass spectrographic analyses of the reaction products. The exothermicity of this flame reaction is governed by the reaction



The volumetric reaction rate ($\dot{M}_{\text{fu,max}}''''$) and heat release rate (\dot{q}_{max}'''') for this reaction are $1.95\text{g/cm}^3\text{-sec}$ and $7.6 \times 10^3 \text{ cal/cm}^3\text{-sec}$, respectively.

I. INTRODUCTION

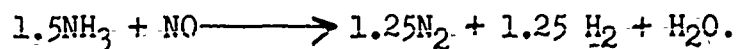
The objective of the research being conducted under this contract, funded by the Advanced Research Projects Agency, is to obtain a better understanding of the mechanisms of combustion, decomposition, and detonation of solids. Current investigations are concerned with the gas-phase reactions associated with the combustion of composite solid propellants and their relationships to the energy transport processes near the solid-propellant surface.

II. TECHNICAL STATUS

A. SUMMARY OF PREVIOUS WORK

Apparent flame strength measurements were made on ammonia-nitric oxide and ammonia-nitrous oxide flames in the opposed-jet reactor at pressures ranging from 100 to 745 torr. The pressure dependencies of the apparent flame strengths gave overall reaction orders of 1.56 and 2.0 for $\text{NH}_3\text{-NO}$ and $\text{NH}_3\text{-N}_2\text{O}$ counter-flow diffusion flames, respectively.

The overall stoichiometry of the $\text{NH}_3\text{-NO}$ flame reaction was deduced from mass spectrographic data and opposed-jet reaction parameters. The stoichiometry can be represented by the equation



The volumetric reaction rate ($\dot{M}_{fu,\text{max}}''''$) for this flame reaction was computed, using Spalding's analysis, to be $2.93 \text{ gm/cm}^3\text{-sec}$ at 1 atmosphere pressure. This corresponds to a volumetric heat release rate of $7.22 \times 10^3 \text{ cal/cm}^3\text{-sec}$.

B. CURRENT AND PLANNED WORK

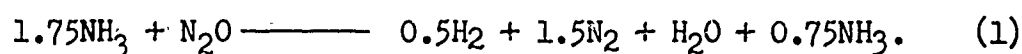
The gas-phase reactions which are believed to occur above the surface of burning composite propellants containing ammonium perchlorate (Reference 1) are being investigated. Current experimental studies are concerned with the overall stoichiometry of the counter-flow diffusion flame between ammonia and nitrous oxide. These flames are being investigated by means of the opposed-jet technique, which has been described previously (References 2 and 3).

1. Combustion of Ammonia with Nitrous-Oxide

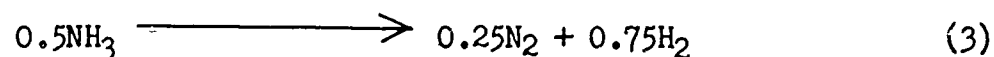
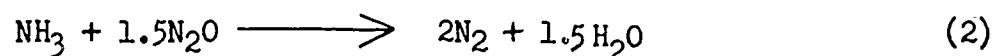
Experimental studies are in progress on the determination of the stoichiometry and exothermicity of the ammonia-nitrous oxide diffusion flame in the immediate region of flame extinguishment. The results of mass spectrographic analyses of representative samples of reaction products are presented in Figure 1. The samples were taken downstream from the flames and the sampling techniques are such that the values for H_2O concentration are inaccurate. This presents no problem since the data indicate that essentially all of the oxygen in the reaction products appears in the water.

The data indicate that unusually large amounts of unreacted ammonia passed through the reaction zone of these flames. This finding was unexpected, since this phenomenon was not observed in other counter-flow diffusion flames between ammonia and oxidants such as O_2 , Cl_2 and NO . Also burning velocity measurements on binary mixtures of NH_3 with N_2O give no indication of any unusual behavior which might distinguish this flame from those between NH_3 and the oxidants mentioned above. The only unusual feature of the NH_3 - N_2O counter-flow diffusion flame that distinguished it from those studied previously is that the flame had a bell shape rather

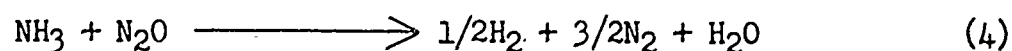
than the usual flat disc shape. Furthermore, the flame extended downward from the mouth of the oxidant jet rather than remaining suspended between the two jets as was normally observed for counter-flow flames. Whether or not these phenomena have any bearing or effect on the nature of the reaction zone, and consequently, on the passage of NH_3 through it, the fact remains that the analytical results are in agreement with the results obtained for the fuel/oxidant ratio as determined from reaction parameters in apparent flame strength (AFS) measurements (Reference 4). The average value of the fuel/oxidant ratio deduced from the H_2/N_2 and NH_3/N_2 ratios listed in Figure 1 is 1.75 which agrees with the value of 1.74 determined from AFS measurements (Reference 4). On the basis of these results and the data listed in Figure 1. The complete reaction is best represented by the equation



However, subtracting out the unreacted NH_3 leaves an overall stoichiometry for the NH_3 - N_2O counter-flow flame that can be represented by the sum of equations (2) and (3).



These equations (1, 2, and 3) indicate that the stoichiometric proportion (1 mole) of NH_3 was oxidized to the expected products, excess NH_3 (0.5 mole) was decomposed into N_2 and H_2 , and finally, that 0.75 mole of NH_3 did not react. Thus, the exothermicity of the flame reaction is governed by the overall reaction



with a corresponding $\Delta H = -3898 \text{ Cal./gmNH}_3$.

The volumetric rate of reaction of ammonia for reaction (4) was calculated on the basis of Spadling's analysis of opposed-jet flames (Reference 5) by the expression

$$\dot{M}_{fu,max}''' = \frac{\rho_{\infty} (f_{\infty} U_{ext})}{\rho_{\infty}} \frac{M_{fu,\infty}}{2\bar{\Psi}_{st}} \frac{\Omega_{st}^2}{f_{st}} \quad (5)$$

where

$\dot{M}_{fu,max}'''$ = the maximum volumetric rate of consumption of fuel (g/cm³-sec)

ρ_{∞} = density of the fuel

f/f_{∞} = fractional density of the fuel in the local mixture (0.33)

$f_{\infty} U_{ext}$ = AFS at 1 atmosphere (laminar flow) = 2.35 gr/cm²-sec

D = jet diameter (0.77 cm)

$M_{fu,\infty}$ = mass fraction of fuel in the fuel stream = 0.57

f_{st} = stoichiometric mass fraction of fuel in the local mixture = 0.41

Ω_{st} = a dimensionless function of f indicative of the burning rate in the flame = 0.938

$\bar{\Psi}_{st}$ = a dimensionless reaction-rate function 0.25

Substitution of the above values into equation (5) yields a value for $\dot{M}_{fu,max}''' = 1.95 \text{ gm/cm}^3\text{-sec}$ for the $\text{NH}_3\text{-N}_2\text{O}$ flame at 1 atmosphere. This value corresponds to a volumetric heat release rate (\dot{q}_{max}''') of $7.6 \times 10^3 \text{ cal/cm}^3\text{-sec}$.

2. Theoretical Studies

A theoretical treatment of extinction phenomena in opposed-jet diffusion flames has been developed which differs from that given by Spalding (Reference 5). In this treatment, maximum reaction rates are determined by means of physical extinction criteria which are imposed

on the flame process rather than previous or assumed chemical kinetic information as required by Spalding's treatment. The results of these studies will be presented in the next report.

3. Publications

A paper entitled "Surface Rate Processes and Sensitivity of Solid High Explosives", by R. F. Chaiken and F. J. Cheselske was submitted for publication in the Journal of Chemical Physics.

4. Future Work

Additional flame studies of the reaction of ammonia with nitrogen dioxide (NO_2) will be made to determine the overall stoichiometry of this flame reaction.

Theoretical studies of the theory of extinction in opposed-jet diffusion flames will be continued.

III. PROJECT PERSONNEL

During the period covered by this report, the following personnel contributed the indicated portions of their time to the program.

	<u>Time, %</u>
F. J. Cheselske, Principal Investigator	100
R. F. Chaiken, Technical Consultant	30

REACTION PRODUCTS FROM AMMONIA-NITROUS OXIDE FLAMES⁽¹⁾
MASS SPECTROGRAPHIC ANALYSES

Identification Number	Product Composition, Mole %					H_2/N_2 ⁽⁴⁾	NH_3/N_2 ⁽⁵⁾
	N_2	H_2	H_2O ⁽²⁾	NH_3 ⁽³⁾	N_2O ⁽³⁾		
FCS-1 ⁽⁶⁾	53.3	14.4	0.8	29.7	1.8	0.27	0.56
FCS-2 ⁽⁷⁾	57.1	16.0	0.8	26.1	-	0.28	0.46
FCS-3 ⁽⁶⁾	56.7	13.8	0.5	27.4	1.6	0.24	0.48

(1) Pressure = 450 torr

(2) These values are inaccurate due to sampling technique

(3) Unreacted

(4) Average value = 0.26

(5) Average value = 0.50 (corresponds to 0.75 moles NH_3 in products)

(6) Samples taken at extinguishment (∞U_{ext})

(7) Sample taken at 0.8 (∞U_{ext})

REFERENCES

1. Twelfth and Thirteenth Quarterly Reports under Contract AF 49(638)-851 dated 31 December 1962 and 31 March 1963; program entitled, Investigation of the Mechanisms of Decomposition, Combustion and Detonation of Solids.
2. A. E. Potter and J. N. Butler, ARS Jour., 54-60 (1959).
3. E. Anagnostou and A. E. Potter, "Flame Strength of Propane-Oxygen Flames at Low Pressures in Turbulent Flow," Ninth Symposium (International) on Combustion, Academic Press, New York 1963, pp. 1-6.
4. Nineteenth Quarterly Report under Contract AF 49(638)-851, dated October 1964; entitled, Investigation of the Mechanisms of Decomposition, Combustion and Detonation of Solids.
5. D. B. Spalding, ARS Jour., 31, 763 (1961).